Analysis Of Safety Behaviors And Failure Mechanisms for Lithium-ion Batteries in Abuse Tests

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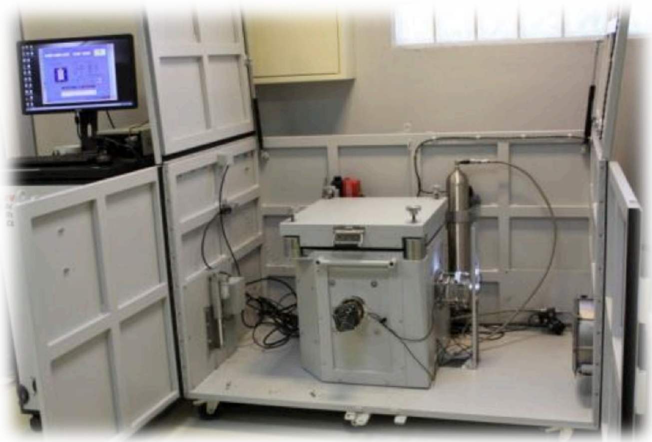
Outline

- **Key safety concerns in lithium-ion batteries (LIBs)**
- **Study of failure mechanism(s) in LIB abuse testing**
  - Internal Short Circuit Simulation test
  - Overcharging test
  - Thermal Abuse Test
- **Summary**

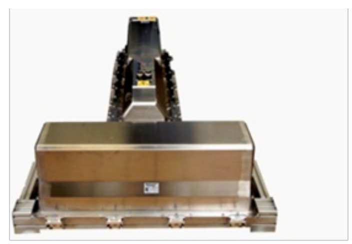


Key Safety Concern(s) in Lithium-ion Batteries

- Three major safety concerns while using a LIB
  - Internal Short-Circuit → No effective way to completely avoid
  - Thermal Abuse → Some materials inside LIB are flammable
  - Overcharging → LIB materials are extremely active under high cell potential
- Emerging Safety Concern(s): Higher power requirement, higher power density, more severe environment, longer service life, etc.

Single Cell Pack
Cell Phone
1-3 years life

6-12 Cells in a Pack
Laptop
1-3 years life

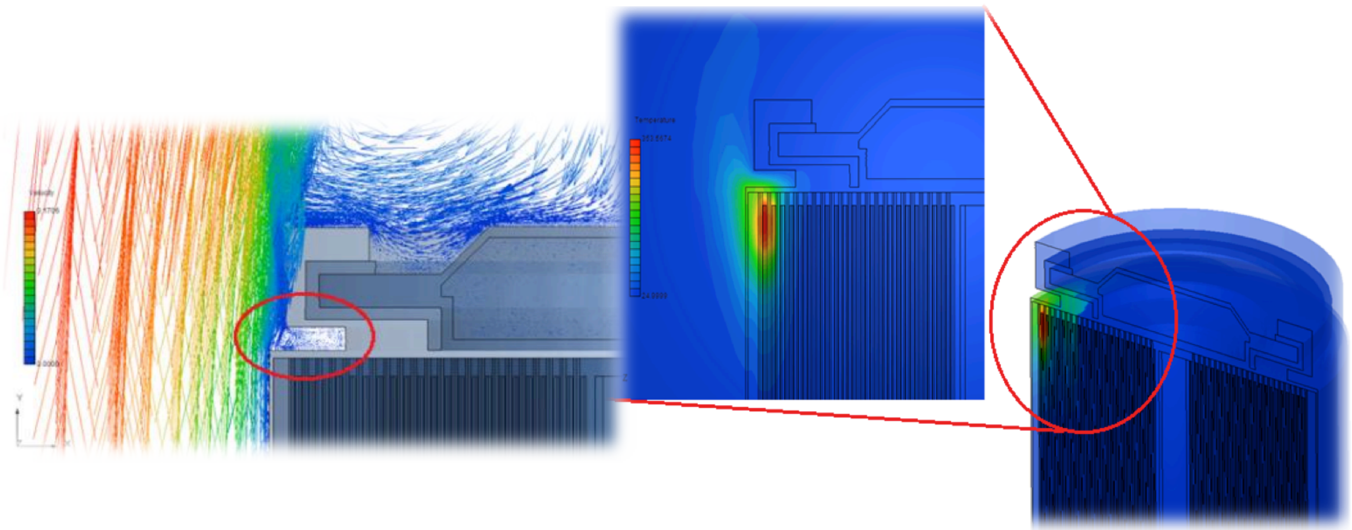


100-5000 Cells in a System
EV/HEV and Motive
5-15 years life

>1000 Cells in a System
Energy Storage and Stationary
10-20 years life

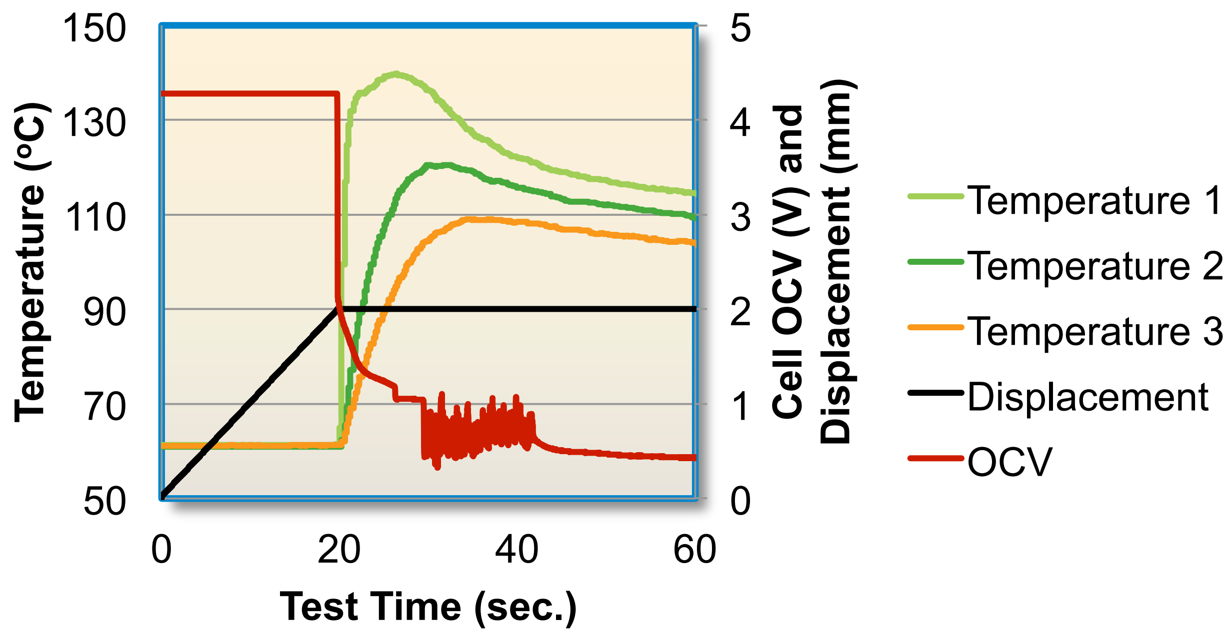
Key Characteristics of ISC Event

- Most ISC events start from localized heating, due to multiple factors, such as manufacturing flaws, mechanical abuse, etc.
- Once the ISC triggers, all safety designs outside of cells are not effective
- Most safety devices within single cell will be also bypassed (ex. fuse, PTC, CID, etc…)

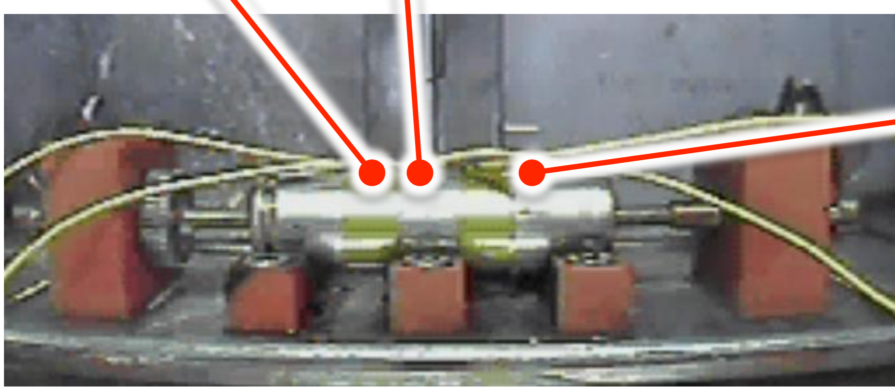


Behaviors Observed from ISC Test

Temperature 1: Closest to ISC point
Peak:
139°C at 25 sec



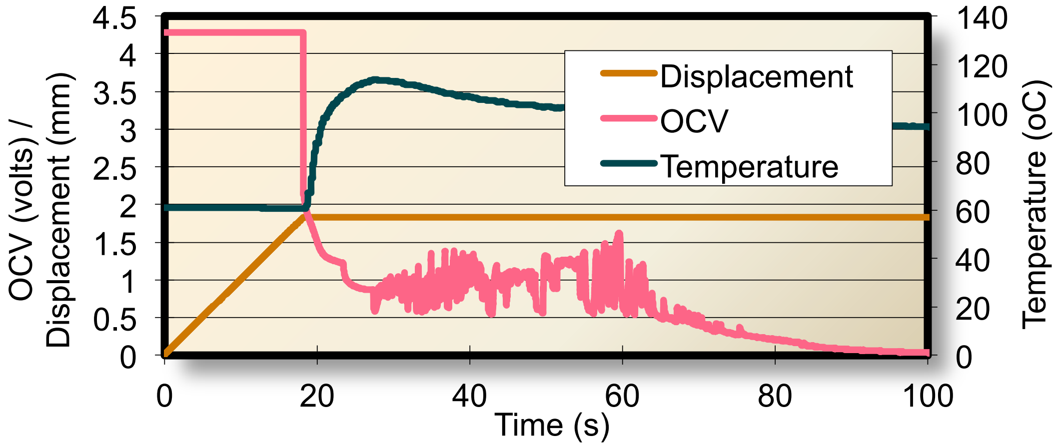
Temperature 2:
Peak:
120°C at 32 sec

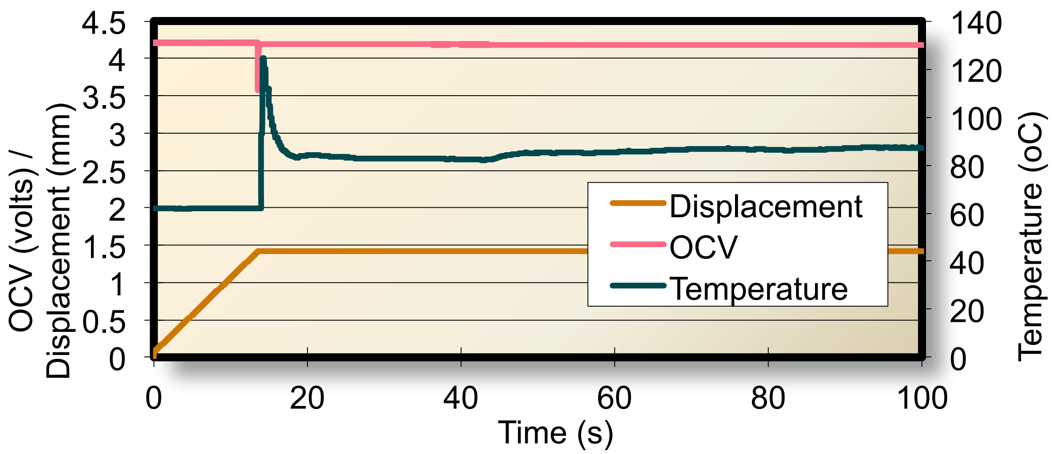


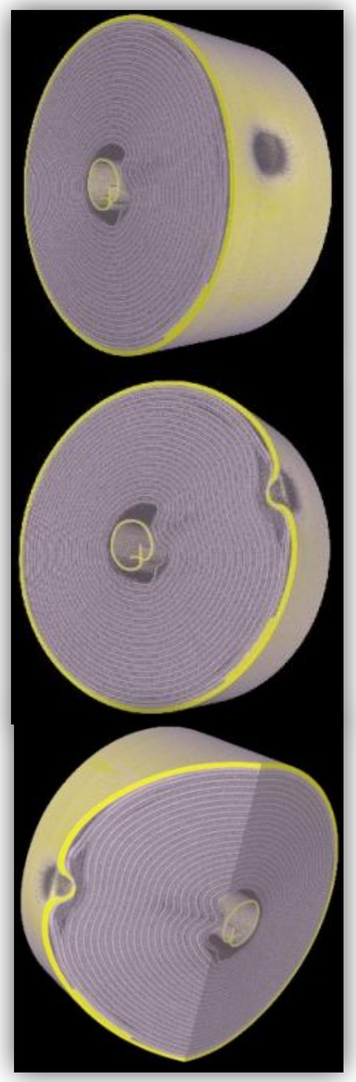
Temperature 3: Farthest to ISC point
Peak:
109°C at 34 sec

Overheating is distributed from ISC point to surrounding area!

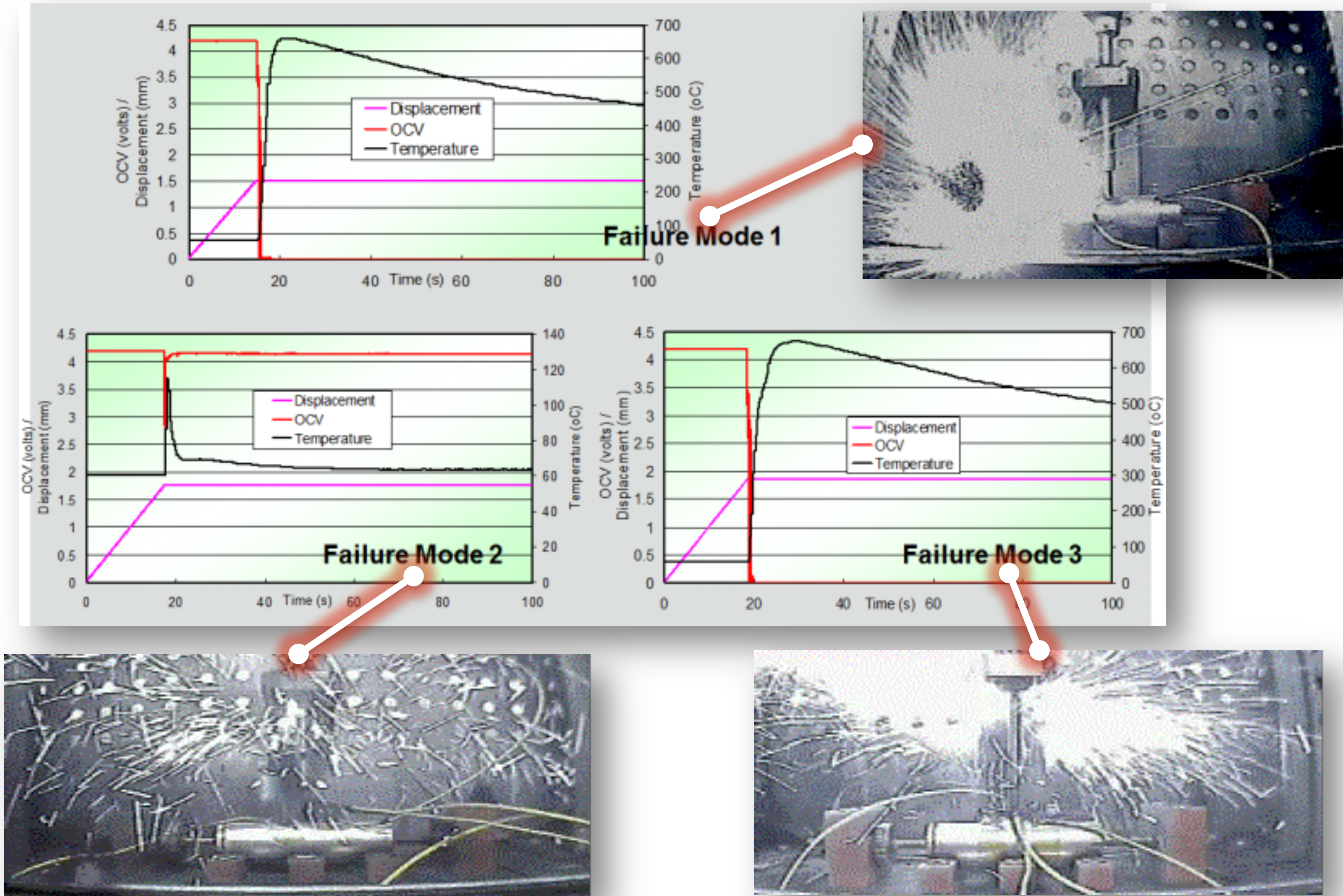
Observed Failure Modes via ISC test







Observed Failure Modes via ISC test (Cont.)



Typical Failure Mechanism in an ISC

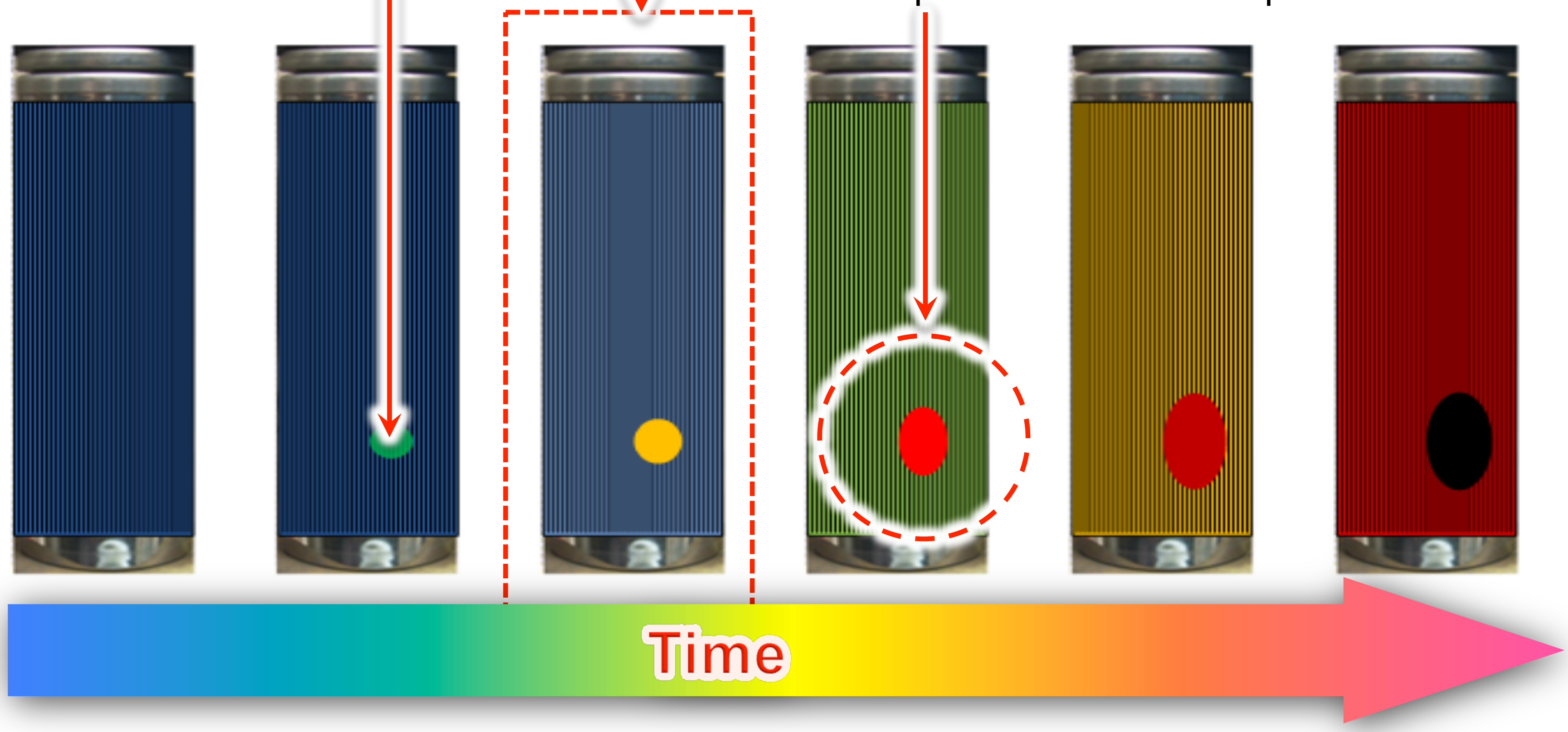
Localized over-heating by Joule Effect at ISC point

$$P_{Electrical} = IV = I^2R$$

Global heating due to the electrochemical reaction

$$P_{Electrochemical} = I(V_{ocv} - V_{op}) + IT\left(\frac{\Delta V}{\Delta T}\right)$$

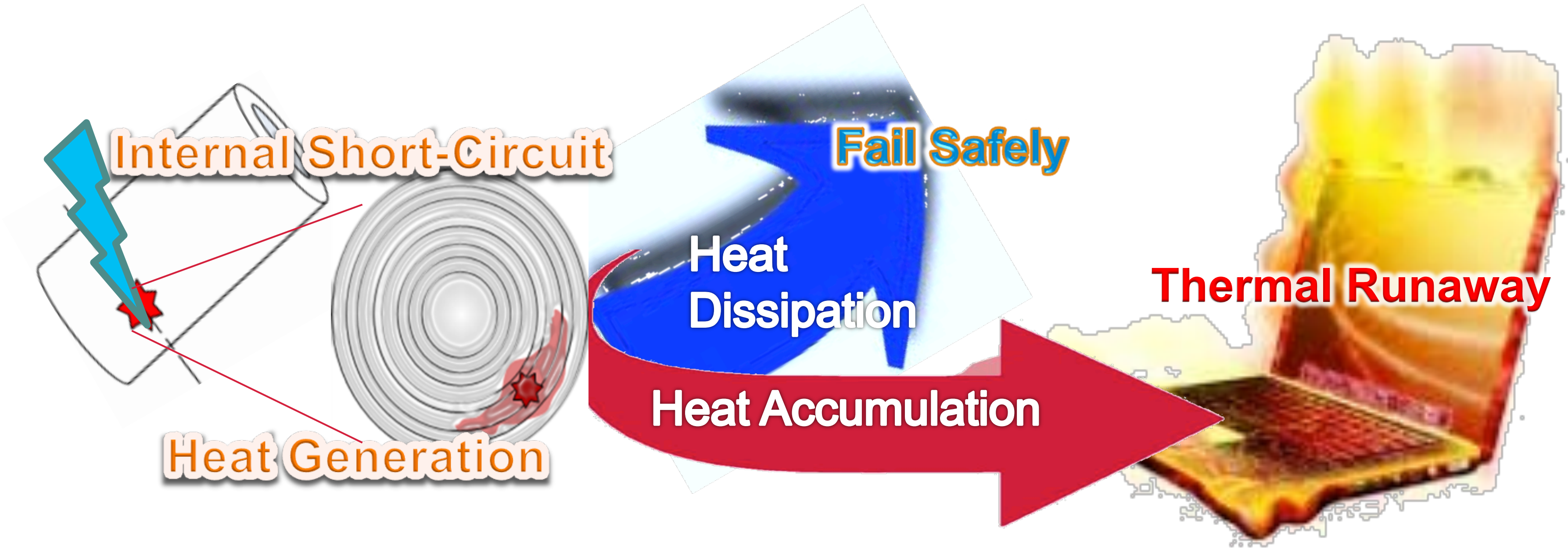
Local over-heating to trigger material decomposition around ISC point



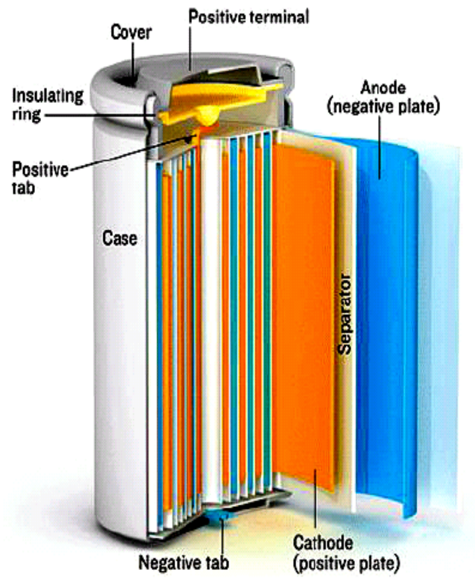
Factors to Cause Thermal Runaway in an ISC Event

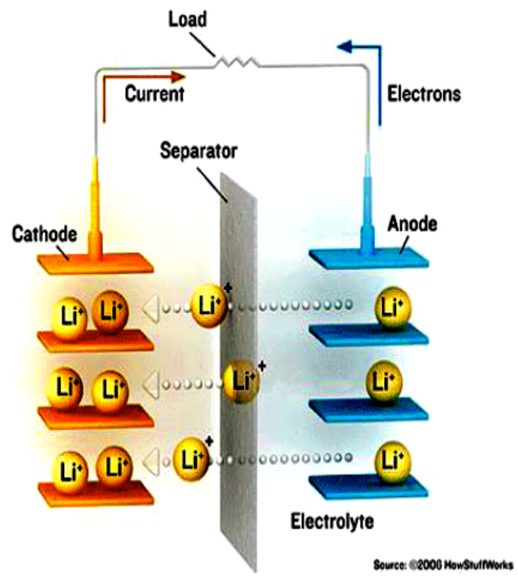
2 Key Factors to “Fail Safely” or “Thermal Runaway” in an ISC event:

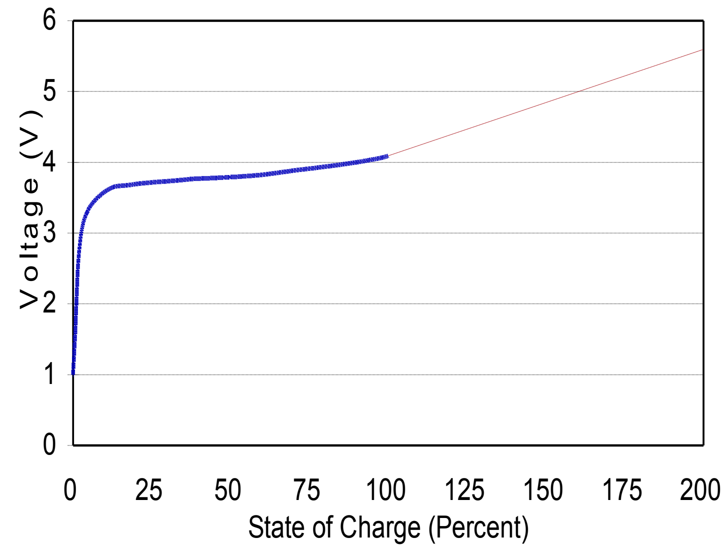
- Heat Generation Rate
- Capability of the Cell Design to dissipate excess heat in short time



Safety Concern of LIB under Overcharge Condition

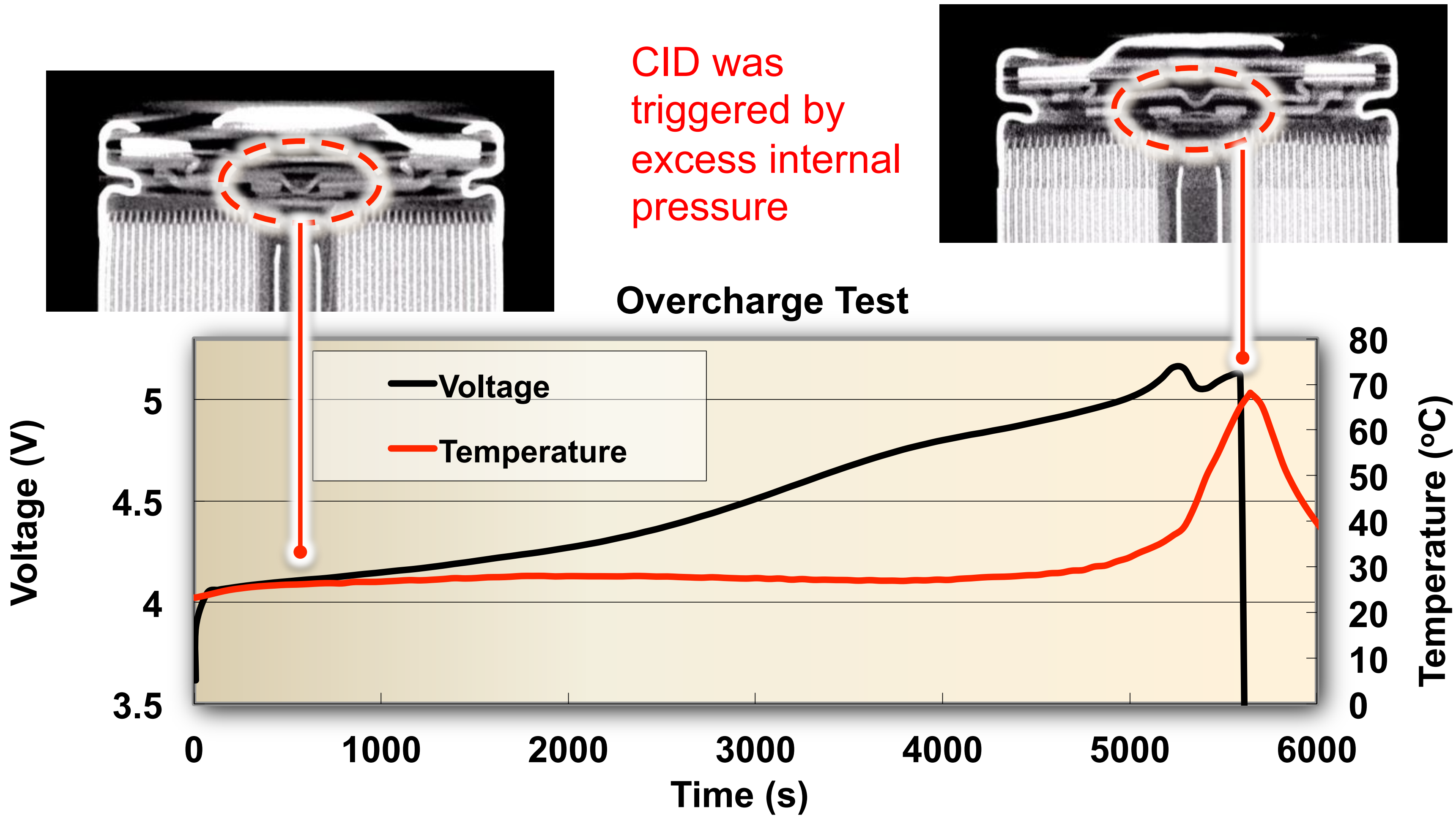






	Discharged		Charged		Overcharged
Cathode	$2LiCoO_2$	⇨	$2Li_{1/2}CoO_2$	⇨	$2CoO_2$ (**O_2**)
Anode	C_6	⇨	LiC_6	⇨	LiC_6 + **Li**

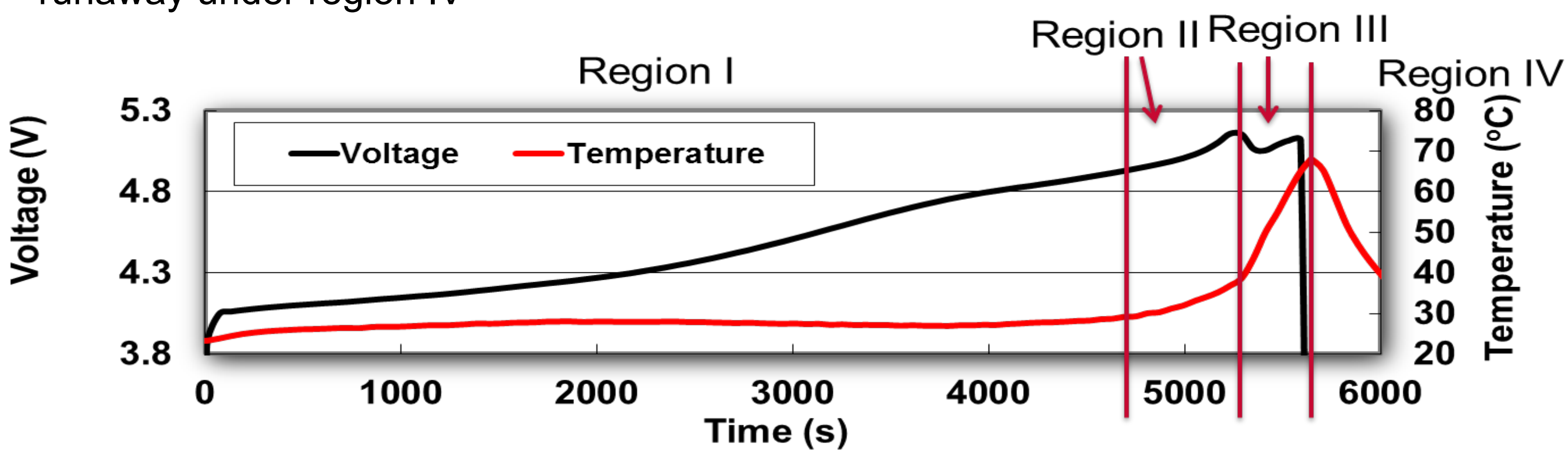
$LiCoO_2$ LIB Behavior(s) under Overcharge Test



If CID is disabled, $LiCoO_2$ type LIB will usually result in thermal runaway after cell voltage is higher than 5.0 to 5.4V due to the abundant heat generated via the violent reaction of electrolyte material with electrodes

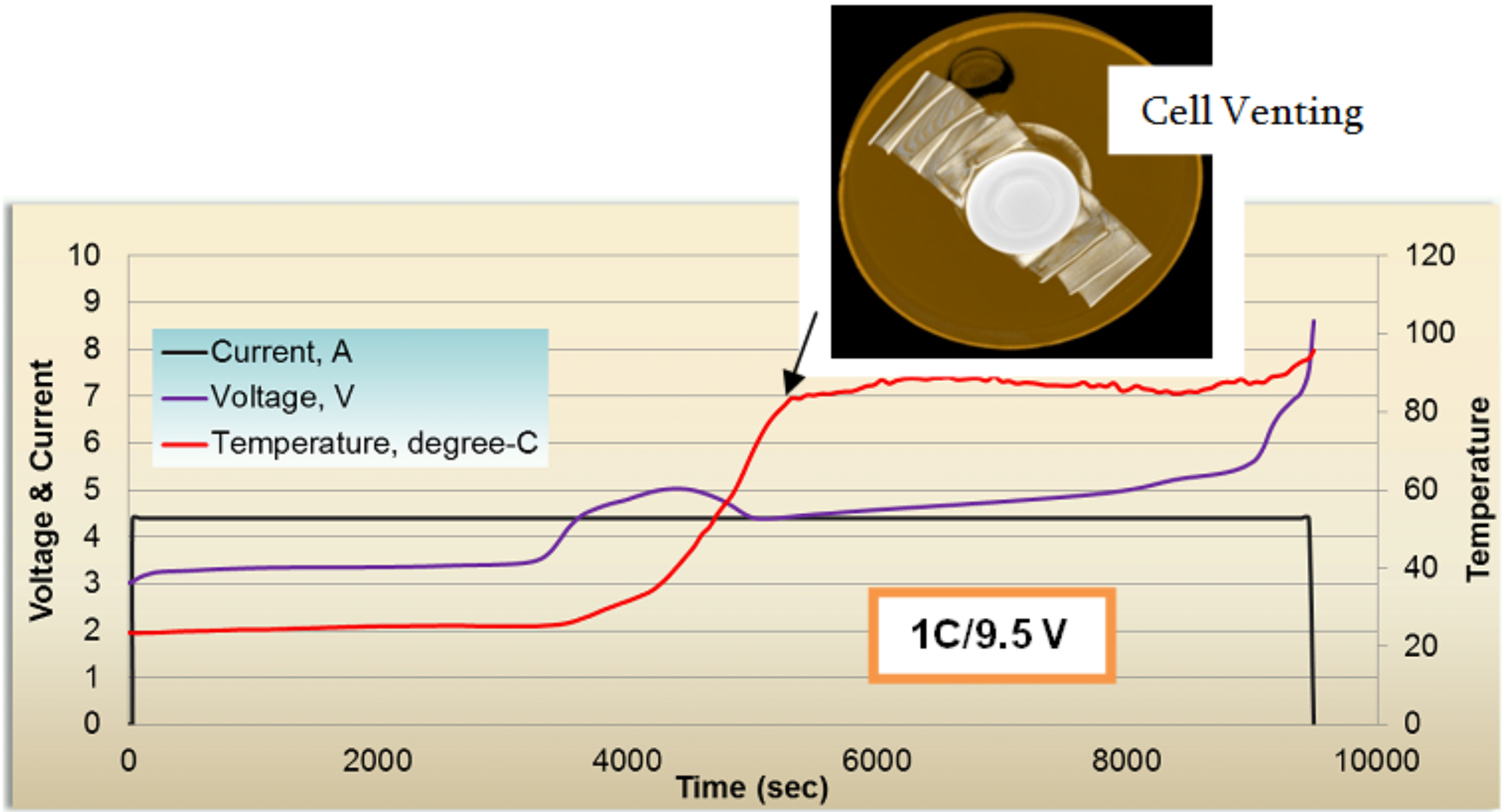
Typical Failure Mechanism in Overcharge Test

- **Region I:** Small temperature rise. Depends on cell anode-to-cathode balance design, lithium metal can be deposited on anode.
- **Region II:** Temperature begins to rise at a slow rate. Electrolyte oxidation can occur at cathode under high voltage. An increase in DC resistance found at around 80 to 95% charge range (i.e. Li_xCoO_2, x=0.2-0.05), but return to a lower value at >95% charge (i.e. x<0.05).
- **Region III:** Temperature begins to rise more quickly. Cell voltage drops and recovers due to the change of cell DC resistance.
- **Region IV:** Cell can fail safely with the aid of CID or other safety devices. However, if there is no effective protection device activated, $LiCoO_2$ type LIB is like to result in thermal runaway under region IV



Source: R. A. Leising et al., J. of The Electrochemical Society, 148 (8) A838-A844 (2001)

LFP LIB Behavior(s) under Overcharge Test



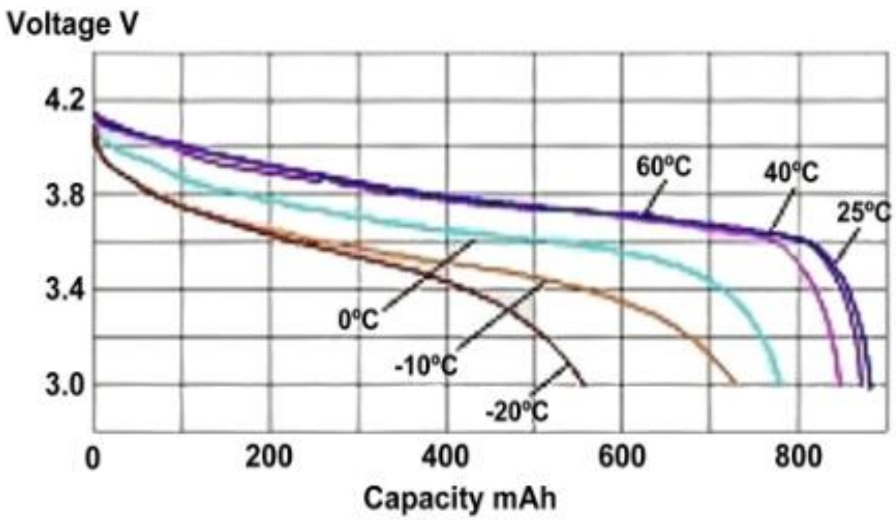
LFP type LIB will not exhibit thermal runaway even under high cell voltage (>9V), because LFP will not oxidize electrolyte materials.

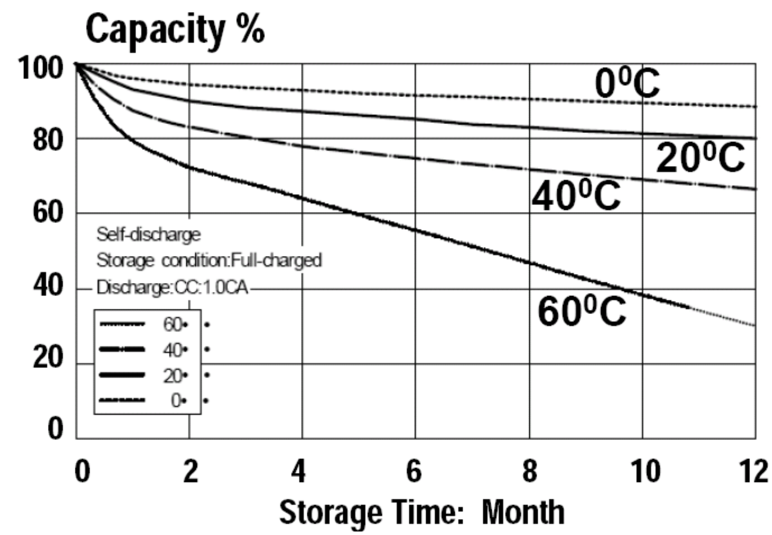
Factor to Cause Thermal Runaway in an Overcharge Event

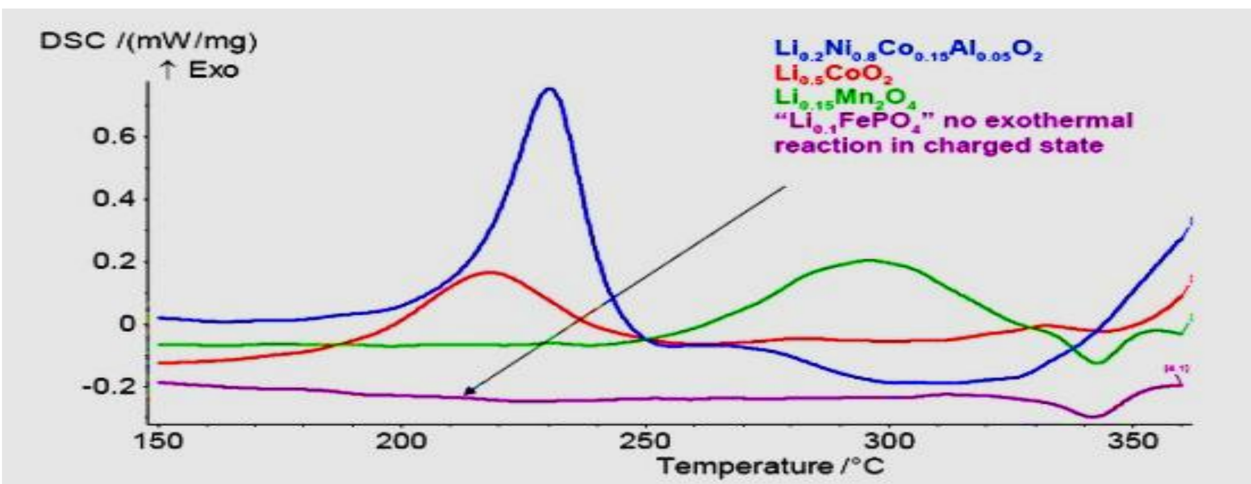
- Material design is the most critical factor

  - $LiCoO_2$ and NMC type LIBs will usually result in thermal runaway after cell voltage is higher than 5.5V (without the aid of protection device(s))
  - $LiMn_2O_4$ type LIBs can possibly fail safely after cell voltage is higher than 10V
  - LFP type LIBs can possibly fail safely after cell voltage is higher than 15V

Temperature is Critical to LIB Performance and Safety

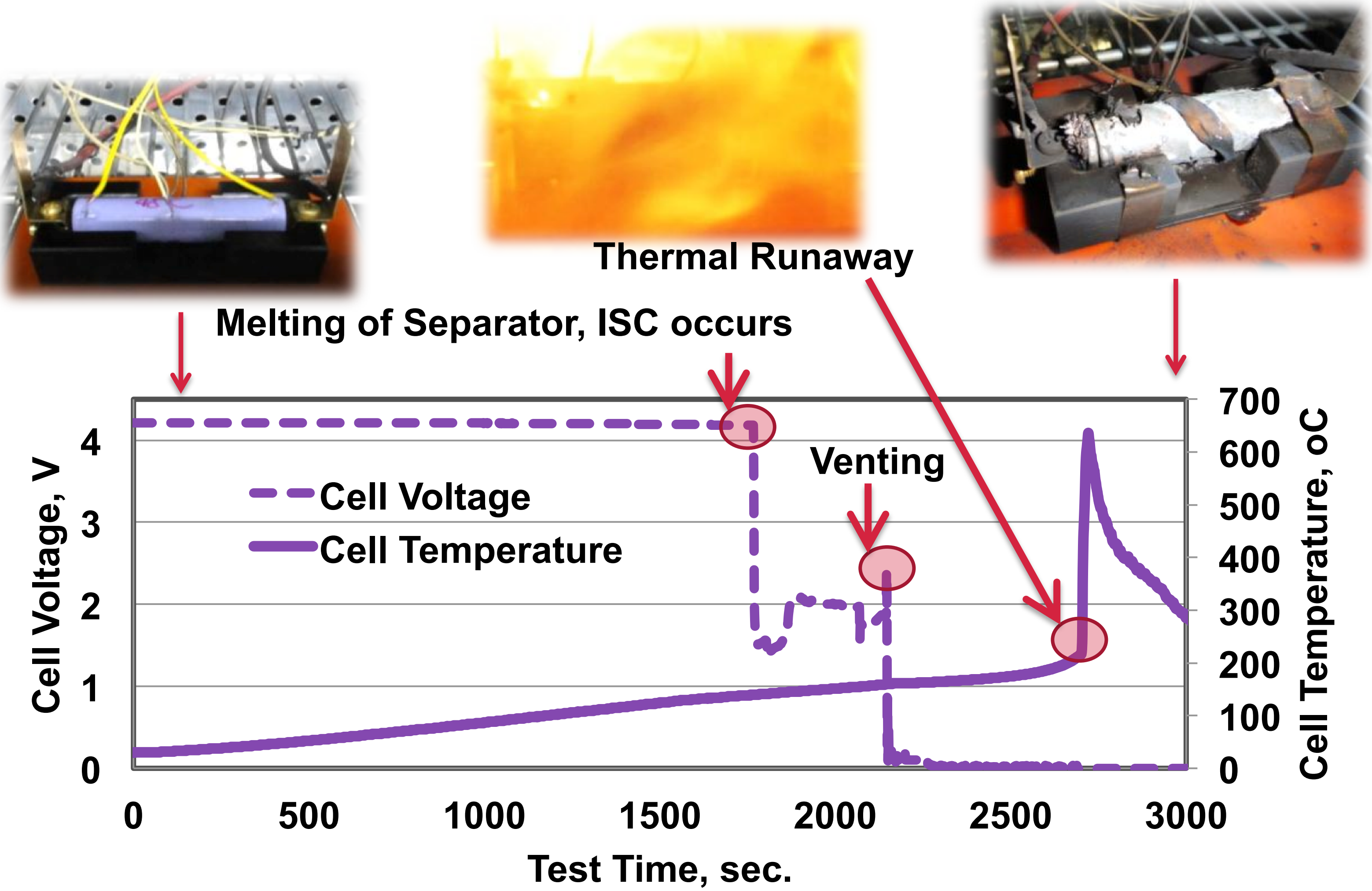






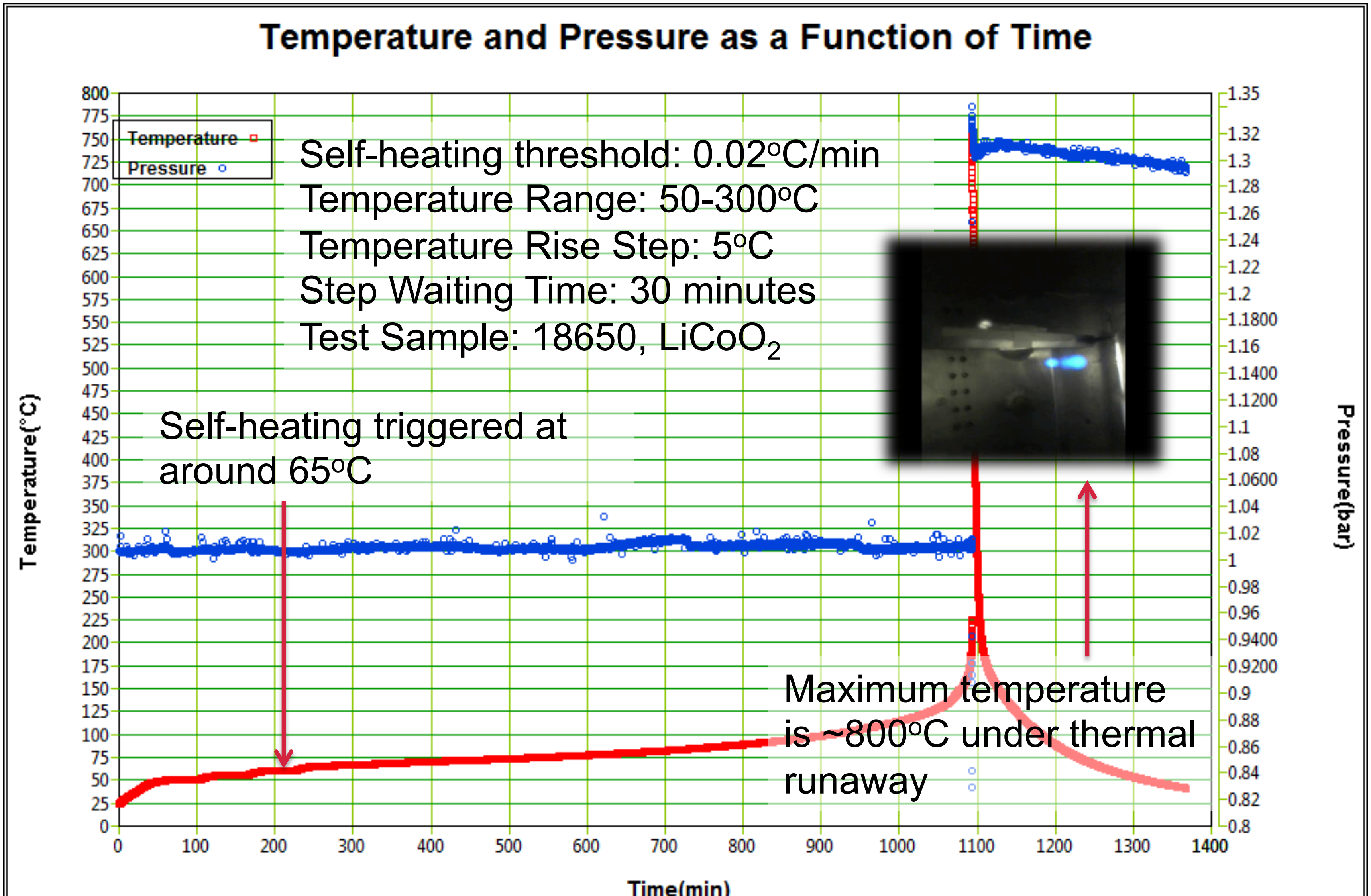
Source: G. Arnold et al. / Journal of Power Sources, 2003, 119–121, 247–251

LIB Behavior(s) in Oven Heating Test

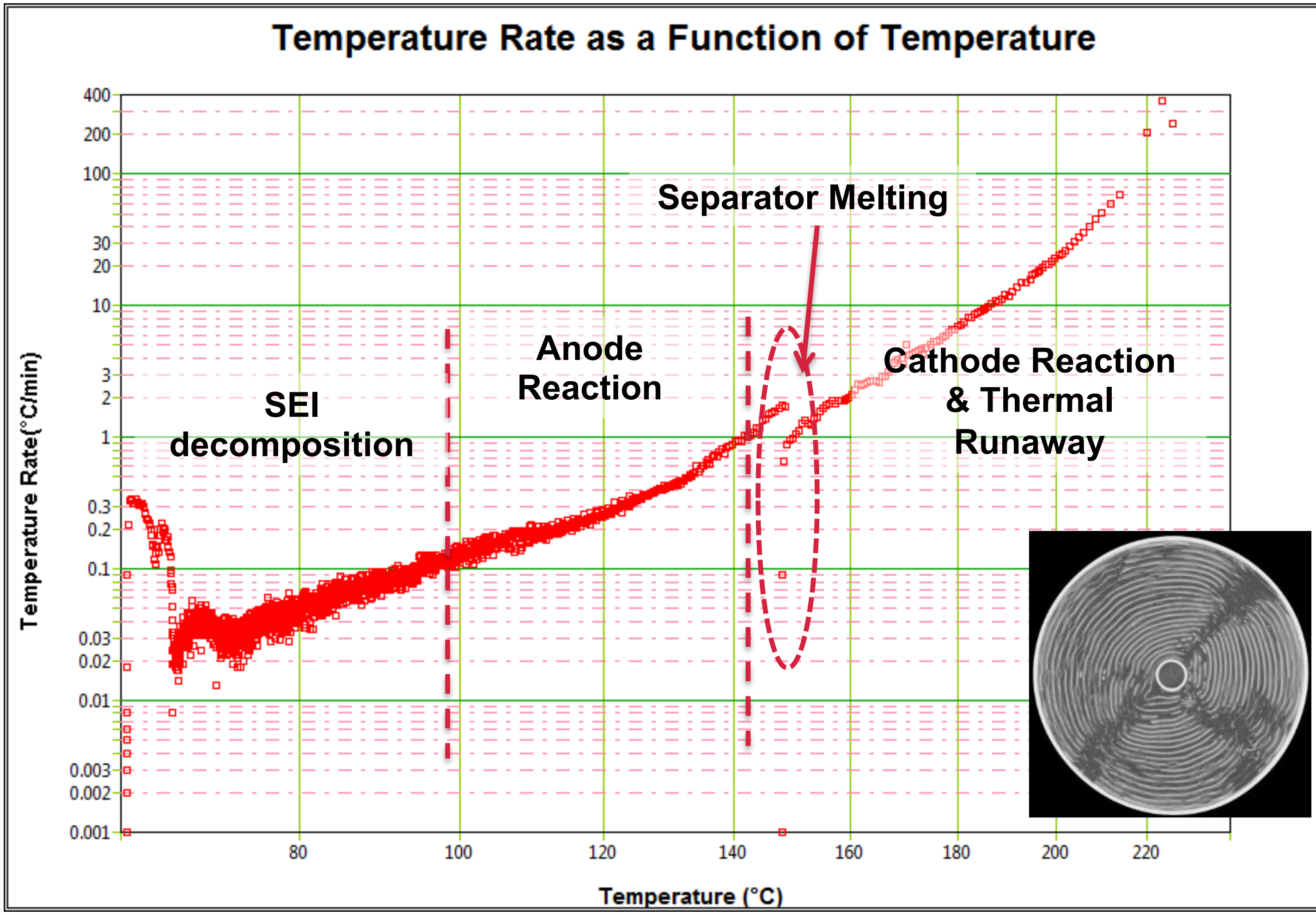


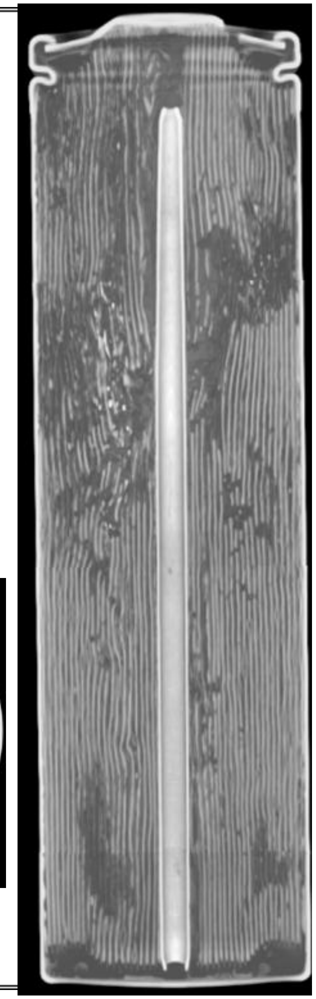
Heating Rate: 5^{o}C/min; from room temperature to 180^{o}C then keep 180^{o}C until thermal runaway

LIB Behavior(s) in ARC Test – 18650 $LiCoO_2$

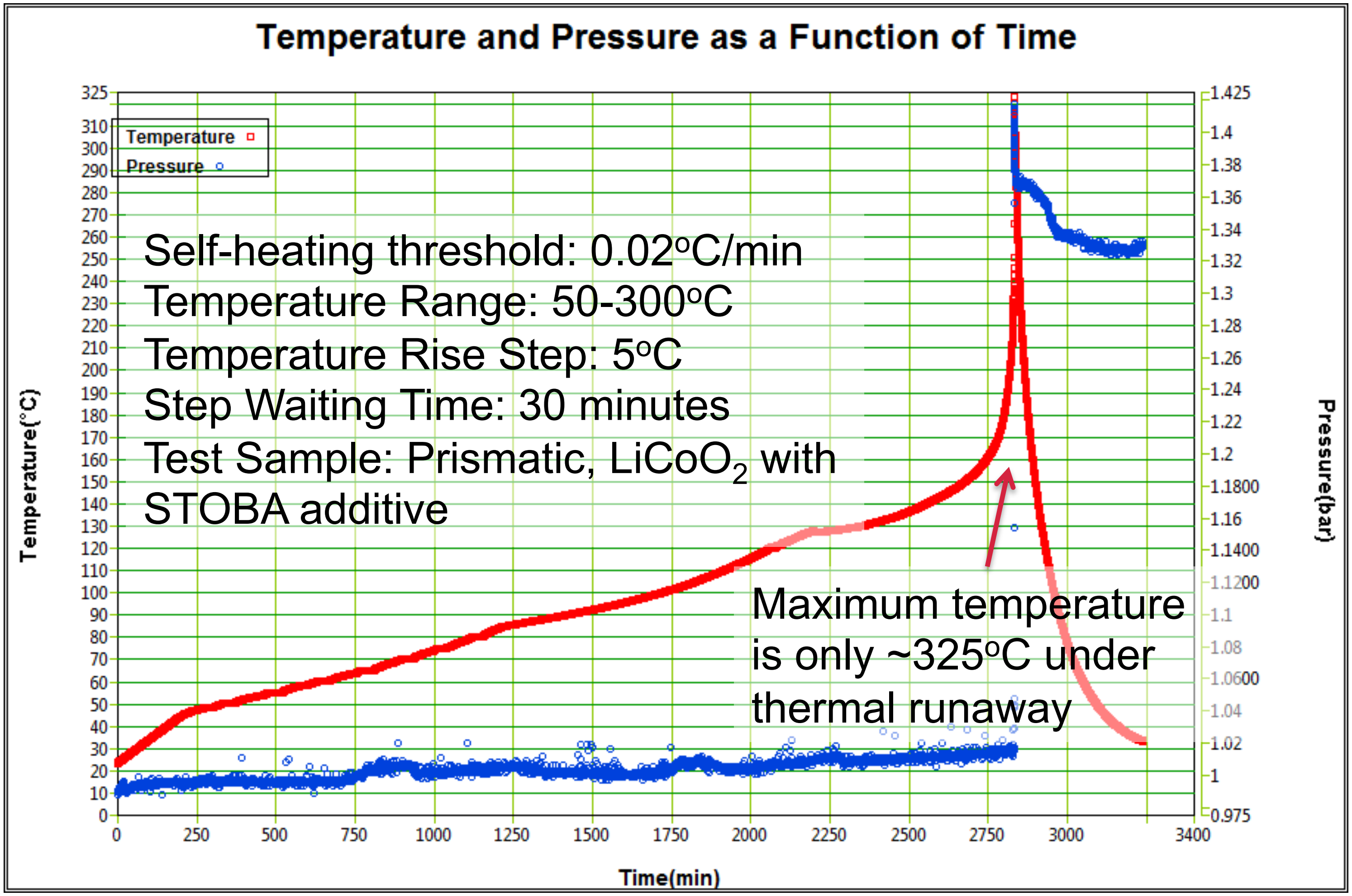


LIB Behavior(s) in ARC Test – 18650 $LiCoO_2$ (cont.)

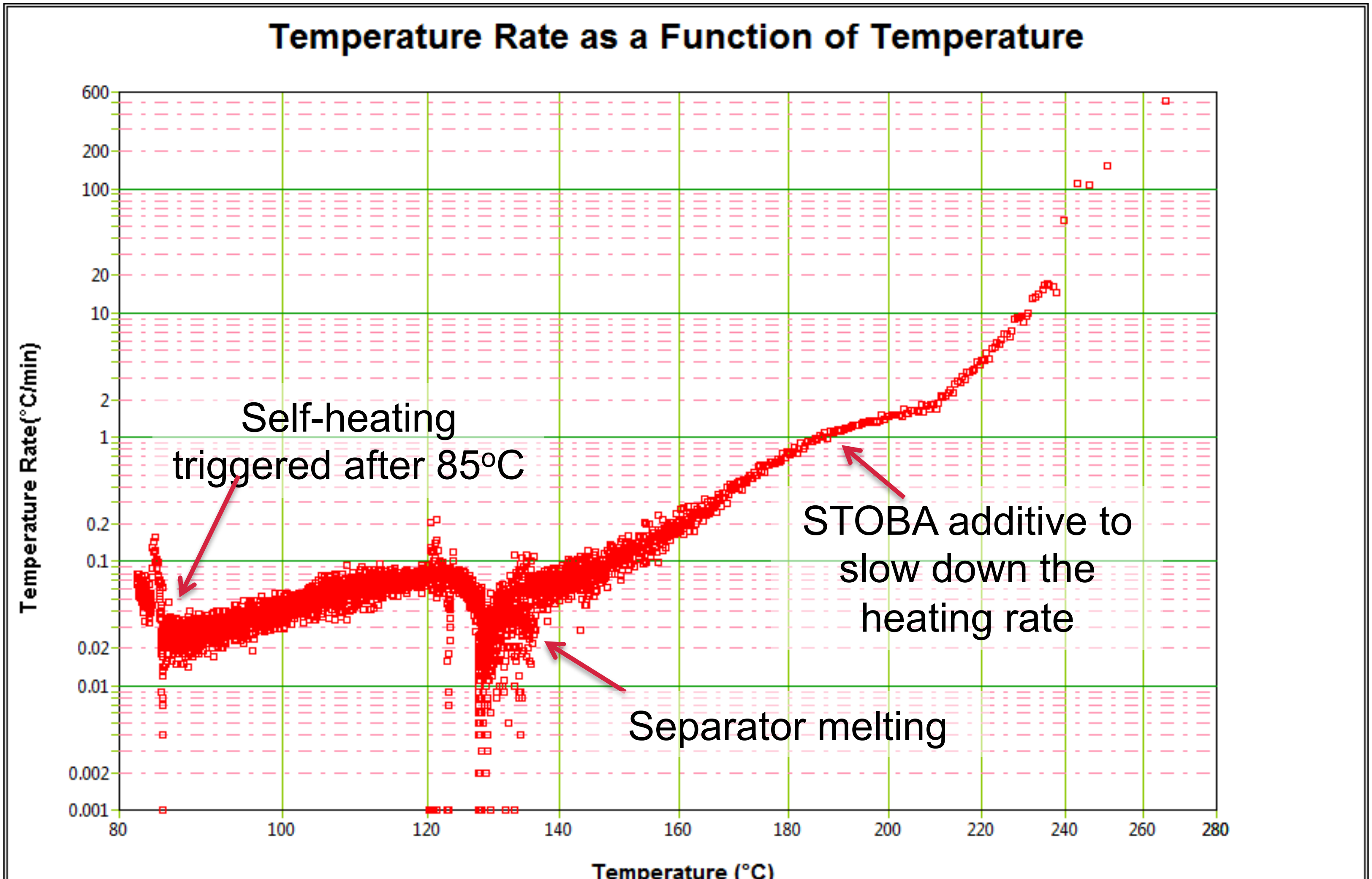




LIB Behavior(s) in ARC Test – Prismatic LiCoO2 with STOBA additive

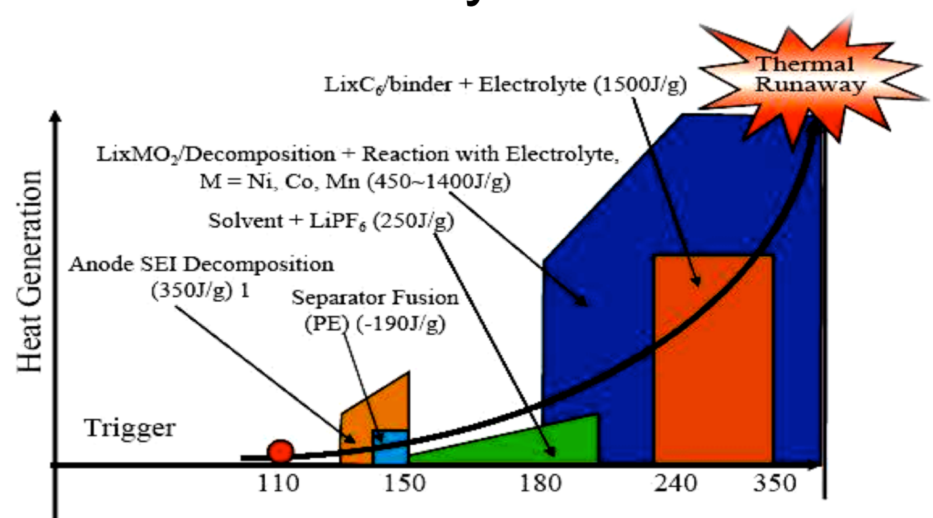


LIB Behavior(s) in ARC Test – Prismatic LiCoO2 with STOBA additive (cont.)



Factor(s) to Cause Self-Heating Chain Reactions in a Thermal Abuse Event

- Poor SEI stability can trigger self-heating at lower temperature (<70°C)
  - The compatibility between anode and electrolyte is critical
- SEI decomposition mechanism is critical at early stage of overheating
- Cathode material is important to the severity of thermal runaway at later stage



Summary

Internal Short-Circuit

- A initial local heating can sometimes introduce a more severe condition because the electrode materials can be still at high chemistry activity at initial stage
- Heat generation and dissipation rate are the two key factors to make cell fail safely or thermal runaway

Overcharge

- Under medium to high voltage region (4.5-5.2V), electrolyte oxidation can occur at cathode and to result in cell swelling
- Under higher voltage (>4.8V), cathode material can possibly decompose to generate oxygen and result in thermal runaway

Thermal Abuse

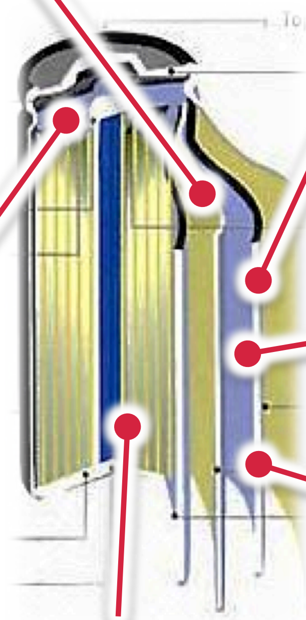
- Thermal stability of SEI is important to minimize the risk of self-heating at early stage of overheating (60^oC-100^oC)
- Anode/electrolyte reactions can generate heat at middle stage of overheating (100^oC-180^oC)
- Separator melting can slow down the self-heating rate (120-160^oC)
- Cathode decomposition can release oxygen and abundant heat at latter stage of overheating (>180^oC)

Example(s) of Strategies to Enhance LIB Safety (Cell Level)

Thicker separator to minimize the risk of ISC and to slow down the heat generation under overheating with the temperature range 120^{o}C-160^{o}C

Coating or fire retardant additives (in electrodes) to enhance the heat dissipation capability and/or to slow down the heat generation while ISC and overheating

Embedded safety devices within cell to break the circuit before the cell voltage goes to a level with high safety risk



Higher A/C ratio to minimize the risk of lithium plating under overcharge condition

Appropriate cathode material design to enhance the cell tolerance to overcharge

Additive (in electrolyte) to stabilize the SEI and electrolyte under overheating

Thank You